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| (54) Title: WATER-DISPERSIBLE GRANULAR AGRICULTURAL COMPOSITIONS (57) Abstract This invention comprises three types of pesticidal granules containing a principal heat-activated binder (HAB) selected from polyethylene glycol, polyethylene oxide, polyethoxylated fatty acids and alcohols, ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols. The granules can be in the form of agglomerates, extrudates or pastilles. | | |

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TITLE

WATER-DISPERSIBLE GRANULAR AGRICULTURAL COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

5 This is a continuation-in-part of USSN 07/899,405
filed June 16, 1992.

This invention relates to new advantageous granular
formulations of active pesticides which are easily
dispersed or dissolved in water for application by
10 spraying or which may be applied as a granular
formulation directly.

Formulation of active pesticides as water-
dispersible powder compositions which can be readily
mixed with water and applied by means of a spraying
15 apparatus to a locus to be protected are generally
dusty, and unpleasant to handle. Granular compositions
have become very popular in recent years because they
are safer and more convenient to handle than wettable
powders.

20 World Patent WO 89/00079 discloses an extrusion
process to make water-dispersible granules of agricul-
tural chemicals in which water is added to make an
extrudable wet mix. The extrudate is rolled to break
the product down to granules and then optionally dried.

25 WO 91/13546 discloses pesticidal, agglomerate-type
granules. Several single component heat-activated
binders (HAB's) are exemplified but not polyethylene
glycols (PEG's). PEG's are mentioned as suitable co-
binders, but none are specifically disclosed. In
30 addition, PEG alone does not satisfy the requirement
specified in WO 91/13546 that the hydrophile/lipophile
balance (HLB) of the HAB be 14 to 19.

U.S. 5,013,498 teaches the preparation of small
pastilles by forcing viscous materials through small
35 apertures in a container into cyclical direct contact

with a moving surface, for example, a cooled steel conveyor belt.

SUMMARY OF THE INVENTION

The present invention pertains to rapidly
5 disintegrating water-dispersible agricultural granular compositions in the form of pastilles, agglomerates and heat extrudate granules comprising by weight based on the total weight of the composition:

- 1) 0.01-90%, preferably 0.03-80%, and most
10 preferred 5-75% of one or more active ingredients;
- 2) 1-90%, preferably 5-60%, of one or more water-soluble heat-activated binder (HAB) selected from polyethylene glycol of average molecular
15 weight 6000 to 10,000; polyethylene oxide; polyethoxylated fatty acids or alcohols; ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols; and
- 3) optionally, one or more additives selected from
20 the group consisting of:
 - a) 0-10% anticaking agent(s)
 - b) 0-10% chemical stabilizer(s)
 - c) 0-20% gas generating disintegrant(s)
 - d) 0-10% wicking or swelling disintegrant(s)
 - 25 e) 0-20% dispersant(s)
 - f) 0-5% wetting agent(s)
 - g) 0-80% inert diluent(s)

provided that (i) when the amount of active ingredient(s) and water-soluble heat-activated binder
30 together are less than 100% then one or more of the additives are required to bring the composition to 100%; (ii) when the granular composition is in the form of agglomerates the heat activated binder is selected from one or more of polyethylene glycol of average
35 molecular weight of 6000 to 10,000, polyethylene oxide,

and polyethoxylated fatty acids or alcohols; and (iii) when the granular composition is in the form of heat extruded granule the heat activated binder is selected from one or more of polyethylene glycol of average
5 molecular weight of 6000 to 10,000, ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols.

What is meant by granular is particles whether they be agglomerates, pastilles, or extrudates of a size of
10 from 74 microns (200 mesh) to 8000 microns (8 mm).

The granular compositions of the invention can consist of agglomerates comprising pesticidal particles bonded together by solid bridges of polyethylene glycol. The granular compositions of the invention can
15 also be of the form made by (1) extruding a dry premix through a die or screen at elevated temperature and (2) chopping, milling or otherwise breaking the extruded material to form granules. In addition, the granular compositions of the invention can be in the form of
20 pastilles made by a rotoforming process whereby a molten slurry of the active(s) and optional additives is drop-formed onto a moving cooling belt to form granules.

Another embodiment of the invention is a process
25 for preparing the granular compositions of the invention. One embodiment of the process for preparing the granular compositions is directed to extrusion of a dry premix followed by the breaking of the extrudate to form the granular compositions. No water is added in
30 the extrusion process and therefore no drying of the final products is needed.

The active ingredient is at least one pesticide or chemical used for crop protection. More specifically, active ingredients are selected from the class of
35 herbicides, fungicides, bactericides, insecticides,

insect antifeedants, acaricides, miticides, nematocides, and plant growth regulants.

The water-soluble HAB is at least one component selected from the group comprising polyethylene glycols (PEG's) of average molecular weight between 6000 and 10,000; polyethylene oxide; polyethoxylated fatty acids and alcohols; ethylene oxide/propylene oxide copolymers (e.g., Pluronic® F108 = a block copolymer 80% ethylene oxide of average molecular weight 14600) and polyethoxylated alkylphenols (e.g., Macol® DNP150 = dinonyl phenol with 150 moles ethoxylation). The water-soluble HAB used for compositions involving agglomerated-type granules is one or more selected from polyethylene glycol of average molecular weight between 6000 to 10,000; polyethylene oxides and polyethoxylated fatty acids and alcohols. The water-soluble HAB used for compositions involving heat extruded type granules is a polyethylene glycol of average molecular weight between 6000 and 10,000. The water-soluble HAB used for compositions involving pastille-type granules are one or more selected from polyethylene glycol of average molecular weight between 6000 and 10,000; polyethylene oxide; polyethoxylated fatty acids and alcohols; ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols. The preferred heat activated binder for granular compositions are polyethylene glycols of average molecular weight between 6000 and 10,000. The most preferred HAB is a PEG of average molecular weight 8000.

The process of the invention for preparing a water dispersible agriculturally suitable granular composition in the form of a heat extruded granule comprising by weight based on the total weight of the composition:

(a) 0.01-90% of one or more active ingredients;

- (b) 1-90% of a water-soluble heat-activated binder; selected from polyethylene glycol of average molecular weight 6000 to 10,000, ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols; and
- (c) optionally one or more additives selected from the group consisting of:
- (1) 0-10% anticaking agent(s)
 - (2) 0-10% chemical stabilizer(s)
 - (3) 0-20% gas generating disintegrant(s)
 - (4) 0-10% wicking or swelling disintegrant(s)
 - (5) 0-20% dispersant(s)
 - (6) 0-5% wetting agent(s)
 - (7) 0-80% inert diluent(s)
- provided that when the amount of active ingredient(s) and water-soluble heat-activated binder together are less than 100% then one or more of the additives are required to bring the composition to 100%, said process comprises feeding a dry premix of the ingredients or feeding the ingredients in two or more streams to an extruder with heat supplied either to the premix or the extruder sufficient to soften the heat-activated binder followed by cutting or breaking of the extrudate to form granules.

DETAILED DESCRIPTION OF THE INVENTION

Agricultural pesticide compositions are usually manufactured and sold as liquid or solid concentrates. In recent years, formulations based on water-dispersible granules have become increasingly popular because they offer several advantages over other types of agricultural formulations. For example, they are stable during storage and transport. Often this is a concern with aqueous suspension concentrates that can settle or develop crystals in storage if the active ingredient has slight water solubility. Also, aqueous

suspension concentrates are not suitable for active ingredients which are subject to aqueous hydrolysis. This is not a problem with water-dispersible granules. In contrast to wettable powders, water-dispersible

5 granules are convenient to handle and measure and are relatively dust-free. They avoid the skin-toxicity and odor problems associated with solvent-based formulations such as emulsion concentrates and organic suspension concentrates.

10 Water-dispersible granules of the invention are used by diluting the granules in a mix tank containing water to make a solution or dispersion which can be sprayed. The dispersed particles formed on dilution should be no larger than 50 microns in their largest
15 dimension to avoid nozzle pluggage or premature settling which results in uneven application of the pesticide. It is therefore necessary that all of the components of the formulated product rapidly and completely disperse or dissolve in the dilution water.

20 Optionally, under certain circumstances, these same water-dispersible granules can be used by directly applying them to the target without first pre-dispersing in water. Here too, rapid granule break-up is important so that the active ingredient is released
25 from the granule and becomes available as a pesticide. Very uniform size, shape and density of the granules are also important for application accuracy, as well as good attrition resistance to survive conveying and transport through application equipment.

30 The granular compositions of this invention are prepared by processes advantageous over conventional processes. Conventional methods for preparing water-dispersible granule compositions involve (1) water-spraying in fluidized bed or pan granulation equipment
35 (2) spray-drying (3) dry compaction and (4) extrusion

of a water-wet paste. Granules prepared by fluid-bed, spray-drying, pan granulation and wet extrusion can be formulated to disperse rapidly when diluted in water. However these processes require specialized technology including extensive dust collection systems and a space-consuming and expensive drying operation. Dry compaction generally does not produce fast-dispersing granules and the product is irregular in shape and prone to attrition.

10 The present invention comprises water-dispersible granular compositions which comprise one or more pesticides and certain heat-activated binders. The granular compositions of the invention can be made by preparing agglomerates comprised of pesticidal
15 particles bonded together by solid bridges of the HAB. Advantages of the agglomerate granules are (1) the potential for incorporation of incompatible pesticides in the same granule, (2) low cost, (3) the simple process required to prepare them, and (4) the lack of
20 the need for extensive dust collection systems and a space-consuming and expensive drying operation.

 Compositions of the instant invention can also be made by extruding a dry premix through a die or screen at elevated temperature and chopping, grinding or
25 otherwise breaking the extruded material to form granules. Advantages of the process involving extruding is that the extruded granular compositions include (1) rapid disintegration and good dispersion properties in water, (2) good attrition resistance, (3)
30 more uniform size and bulk density than granules prepared by fluid-bed or pan granulation or by other tumbling/mixing processes such as in a rotating drum granulator, (4) simple process which uses readily available commercial extruding equipment, and (5) no
35 need for drying or dust collection equipment.

The granular compositions can also be pastilles made by a rotoforming process whereby a molten slurry of the pesticide(s) and any of the optional additives are drop-formed onto a moving cooling belt. Advantages of the pastille granules include (1) very uniform size, shape and density, (2) hard, smooth non-dusty forms which have good attrition resistance, (3) are prepared by a simple, low-cost manufacturing process, which (4) does not involve costly drying or dust-collection equipment.

The agglomerate granules of this invention are prepared by any of the following processes (either in a batch or continuous mode) whereby (1) the pesticidal particles or active ingredient(s), the HAB particles and optional particulate additives are tumbled/mixed and heat is applied externally until the granules have grown to the desired size, following which the heat is shut-off and the granules are allowed to cool while still tumbling or sitting in a separate container; or where (2) the pesticidal particles or active ingredient(s), HAB, and optional particulate additives are intensely sheared/mixed such that frictional heat softens the HAB thereby effecting granulation following which the aggregates are then cooled; or where (3) the pesticidal particles or active ingredient(s) and optional particulate additives are tumbled/mixed and are sprayed with the HAB which has been pre-heated and is in a molten state following which the resulting agglomerates are cooled.

Processes (1) and (3), involving gentle tumbling/mixing, can be carried out in a heated fluidized bed, a heated blender (e.g., paddle or ribbon type blenders, vee-blenders, zig-zag blenders, Lodige® blenders, Nauta® mixers) or a heated pan or drum granulator. Process (3) may not require additional heat other than

that needed to melt the HAB for spraying. Subsequent cooling of the resulting agglomerates is done either in or outside of the processing vessel. Process (2) involving high intensity mixing/shearing can be carried out, for example, in Schugi® or turbulator-type vessels. In Process (1) a preferred method of preparing the initial mixture of particulates before granulation is to mill the pesticidal active plus additives and then mix (e.g., via tumbling) with HAB particulates (e.g., of a size 10-1,000 microns). Preparation of compositions involving more than one active ingredient can be enhanced and incompatibility reduced (especially when one active is present in minor proportions) by forming granules from a particulate premix of the major active component, HAB, and additives, followed by introduction of the minor active component (and optionally additional HAB), while the granules are hot so as to imbed the second active particulates in an HAB layer on the surface of the first granules.

The granular compositions of this invention can also be prepared by heat extrusion which involves a process comprising preparing an extrudable premix by combining the pesticidal particles with an HAB, e.g., PEG 8000. Other additives may optionally be included in the premix such as wicking, swelling or gas-generating disintegrants, one or more dispersants, and additives such as wetting agents, anticaking agents, chemical stabilizers, and inert diluents.

In one embodiment, the premix is blended and milled to an average particle diameter between 1 and 50 microns. The milled premix is then fed or metered into an extruder that has been heated electrically, by steam, or by other conventional means of heating. Suitable extruders include single and twin screw

models, radial extruders and roll-type extrusion presses. In some types of extrusion equipment, for example, a California Pellet Mill®, the heat can be generated from friction. Other means of heating the premix can include preheating the premix before extrusion, or heating the individual components of the premix before blending. The premix is heated to a temperature in the range of about 45° to 130°C, preferably about 60° to 115°C. The optimum temperature varies with the composition but can be determined empirically. High temperatures which can cause decomposition of the active ingredient should be avoided.

In a preferred extrusion process the powdered premix ingredients are not premilled, but are fed in two or more streams to an extruder (for example a co-rotating or counter-rotating twin screw unit) equipped with screw elements that facilitate dispersive and distributive mixing. The various ingredients of the formulation are blended, sheared, and heated in the extruder, yielding a uniform extruded composition which gives a good quality dispersion when added to water. This approach is highly desirable because it eliminates the dusty process of milling the pesticide formulation. Other embodiments of the process of the invention will be readily apparent. For example, the active ingredient may be separately premilled to obtain an optimum particle size for biological activity, and the extruder is then used to blend the premilled active ingredient and the unmilled formulation ingredients to produce the desired composition.

The heated premix is extruded through a die or screen. The die holes range in diameter from 0.25 to 7 mm, preferably from 0.4 to 2 mm. Depending on the composition and the type of extruder used, the extruded

material can be recycled until the strands are uniform in texture. Generally, the extruded material is allowed to cool to harden and reduce stickiness, although this is not always necessary. The strands are
5 chopped, milled or rolled and then screened to approximately 10 to 60 U.S. mesh size granules. A narrower cut size range can be selected. In some cases the strands are sufficiently brittle that they break on their own into short lengths.

10 The pastille granular compositions of this invention are prepared in the following manner. The active ingredient(s) and any necessary optional additives are blended and milled as necessary to achieve proper spray tank or biological performance.
15 These are then combined with the required amount of HAB in a heated, agitated tank and the temperature of the mixture is raised between the melting point of the binder and that of the other additives. Temperatures acceptable for the process are those above the melting
20 point of the binder and below the decomposition temperature of the ingredients. Temperatures in the range of 90-110°C are preferred. Once the composition is heated and well mixed, it is pumped to a feed device which deposits a precise amount of the mix in droplet
25 form onto a cooling belt for ultimate solidification. A preferred feed device is the Rotoformer® (Sandvik® Process Systems) although other devices such as nozzles, injectors, and the like may be used. Once the pastilles are deposited onto the cooling belt, they
30 remain a sufficient length of time to fully cool and solidify into a hard, non-dusty granule.

The active ingredient should be chemically stable in the temperature range required for preparing the composition. Examples of suitable active ingredients
35 are listed in Table 1.

Herbicides such as acifluorfen, asulam, atrazine, bensulfuron methyl, bentazon, bromacil, bromoxynil, hydroxybenzonitrile, chloramben, chlorimuron ethyl, chloroxuron, chlorsulfuron, chlorotuluron, clomazone, 5 cyanazine, dazomet, desmediphan, dicamba, dichlorbenil, dichlorprop, diphenamid, dipropetryn, diuron, thiameturon, fenac, fenuron, fluometuron, fluridone, fomesafen, glyphosate, hexazinone, imazamethabenz, imazaquin, imazethapyr, ioxynil, isoproturon, isouron, 10 isoxaben, karbutilate, lenacil, MCPA, MCPB, mefluidide, methabenzthiauron, methazole, metribuzin, metsulfuron methyl, monuron, naptalam, neburon, nitralin, norflurazon, oryzalin, perfluidone, phenmedipham, picloram, prometryn, pronamide, propazine, pyrazon, 15 rimsulfuron, siduron, simazine, sulfometuron methyl, tebuthiuron, terbacil, terbuthylazine, terbutryn, triclopyr, 2,4-D, 2,4-DB, triasulfuron, tribenuron methyl, primisulfuron, pyrazosulfuron ethyl, N-[[[4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethyl- 20 sulfonyl)-2-pyridinesulfonamide, nicosulfuron, and ethametsulfuron methyl; fungicides such as carbendazim, thiuram, dodine, chloroneb, cymoxanil, captan, folpet, thiophanate-methyl, thiabendazole, chlorothalonil, dichloran, captafol, iprodione, vinclozolin, 25 kasugamycin, thiadimenol, flutriafol, flusilazol, hexaconazole, and fenarimol; bactericides such as oxytetracycline dihydrate; acaricides such as hexathizox, oxythioquinox, dienochlor, and cyhexatin; and insecticides such as carbofuran, carbyl, 30 thiodicarb, deltamethrin, and tetrachlorvinphos.

The water-soluble HAB dissolve rapidly in water, have some viscosity above their melting point and are capable of acting as a binder when heat is applied. At an elevated temperature the binder softens and melts, 35 becoming sticky enough to bind the active ingredient

particles into larger aggregates. For the heat extruded compositions, it is theorized that the softened or melted HAB can also function as a plastic or viscoelastic lubricant allowing the composition to
5 extrude through a die or screen. For pastilles, the HAB acts as a thermoplastic matrix into which the pesticidal solid particles and other ingredients are dispersed.

The HAB must meet the following four criteria:

- 10 (1) have a melting point range within 40 to 120°C;
- (2) dissolve in mildly-agitated water in 50 minutes or less;
- (3) have a melt viscosity of at least 200 cps; and
- 15 (4) have a difference of 5°C or less between the softening point and onset of solidification.

The preferred HAB of this invention is PEG with an average molecular weight between 6000 and 10,000. The use of a PEG having the specified melt viscosity and minimum difference between softening and solidification
20 temperatures is necessary so that it will be tacky enough to effect agglomeration of pesticidal particles near the melting point of the HAB.

The compositions of this invention optionally include the following additives which are well known in
25 the art:

- (1) Disintegrant(s) which wick in water and physically expand to aid break-up of the granule. Non-limiting examples of suitable disintegrants include starch, cross-linked polyvinylpyrrolidone (e.g.,
30 Polyplasdone® XL-10), microcrystalline cellulose (e.g., Avicel® series), cross-linked sodium carboxymethyl cellulose, sodium starch glycolate, soy polysaccharide and ion exchange resins. Cross-linked polyvinylpyrrolidone and cross-linked sodium carboxymethyl
35 cellulose are preferred.

(2) Dispersant(s) which help disperse the active ingredient in water. Preferred dispersants include sodium and ammonium salts of naphthalene sulfonate-formaldehyde condensates (e.g., Morwet® D425); sodium, 5 calcium and ammonium salts of ligninsulfonates (e.g., Norlig® 11d, optionally polyethoxylated and Polyfon® F); sodium and ammonium salts of maleic anhydride copolymers and sodium salts of condensed phenolsulfonic acid.

10 (3) Anticaking agent(s) which prevent clumping of granules when stored under hot warehouse conditions. Non-limiting examples include sodium and ammonium phosphates, sodium carbonate and bicarbonate, sodium acetate, sodium metasilicate, magnesium, zinc and 15 calcium sulfates, magnesium hydroxide, (all optionally as hydrates), anhydrous calcium chloride, molecular sieves and sodium alkylsulfosuccinates (e.g., Aerosol® OT-B) and sodium and calcium stearates. Foammaster® Soap L is sodium stearate. Non-ionic and anionic 20 surface-active materials which may be soluble in the HAB can also function as anti-caking aids by modifying the melting range and tackiness of the HAB. These may optionally be predissolved or predispersed in molten HAB prior to formulation of the premix. Non-limiting 25 examples include polyethoxylated alkylphenols (e.g., Triton® X-100), polyethoxylated fatty acids or alcohols, and silicone-based surfactants (Silwet® L-77).

(4) Chemical stabilizer(s) which prevent 30 decomposition of the active(s) during storage. Non-limiting examples of suitable chemical stabilizers include alkaline earth and transition metal sulfates such as magnesium, zinc, aluminum and iron, sodium hexametaphosphate, sodium pyrophosphate, calcium 35 chloride and boric anhydride.

(5) Gas producing disintegrant(s) for faster break-up of the granule in water. Non-limiting examples of suitable gas generating additives are combinations of sodium and potassium bicarbonates and carbonates which may be combined with acids such as citric and fumaric acid.

(6) Wetting agent(s) which improve the speed of wetting upon mixing with water. Non-limiting examples of anionic wetting agents include sodium salts of alkyl naphthalene sulfonates (e.g., Petro® Ag-Special), alkyl benzene sulfonates, alkyl sulfosuccinates, taurates, alkyl sulfates and phosphate esters. Examples of suitable nonionic wetting agents include acetylenic diols and alkyl phenol ethoxylates.

(7) Diluent(s), including but not limited to inorganic fillers well known in the art. Non-limiting examples are swelling and non-swelling clays, synthetic and diatomaceous silicas (e.g., Wessalon® 50S), calcium and magnesium silicates, talc, titanium dioxide, aluminum, calcium and zinc oxide, calcium and magnesium carbonate, and charcoal. Non-limiting examples of water-soluble diluents include sodium acetate, ammonium, sodium and potassium sulfate, sucrose, dextrin, urea, lactose, and sorbitol. Water-soluble polymers may be added to improve rheology. Non-limiting examples include methylcellulose, hydroxyethylcellulose, starch, and polyvinylpyrrolidone.

The granules of this invention break-up rapidly and form high quality dispersions in water as determined from the Long Tube Sedimentation test described in U.S. 3,920,442, Col. 9, lines 1 to 39. Acceptable Long Tube Sedimentation values correspond to less than 0.02 mL, preferably less than 0.01 mL, of solids after 5 minutes of settling.

The break-up times in water should be less than 5 minutes and preferably less than 3 minutes. Break-up time is measured by adding a sample of the granules (0.5 g, 74 to 2,000 microns) to a 100 mL graduated cylinder (internal height after stoppering is 22.5 cm; I.D. is 28 mm) containing 90 mL of distilled water at 25°C, following which the cylinder is clamped in the center, stoppered, and rotated about the center at 8 rpm until the sample is completely broken up in the water.

The granules should exhibit low attrition characteristics which can be determined by the attrition test in U.S. 3,920,442 (Col. 8, lines 5-48). The test is modified to use test samples of the commercial granule size (e.g., 74-2,000 microns). Attrition values of less than 40% and preferably less than 30% are acceptable.

The granules should also resist caking. This property is determined by taping a stainless steel disc (0.9 mm thick x 51 mm diameter) to the bottom of a glass cylinder (46.5 mm I.D. x 75 mm length x 51 mm O.D.). Twenty grams of the granular sample is poured into the cylinder assembly and leveled, and a second stainless steel disc (0.9 mm thick x 44.5 mm diameter) is placed on top of the granules. A 390 g weight is then placed on top of the inner disc, and the entire assembly is sealed in a glass jar and placed in a 54°C oven for 1 or 2 weeks. The assembly is then removed from the oven, the weight is removed, and the sample is allowed to cool to room temperature. The bottom disc is then detached and if the sample flows out of the cylinder, the resistance to caking is excellent. If the sample remains in the cylinder, the cake is gently pushed out onto a flat surface and a penetrometer fitted with a single-edged razor blade is used to

measure the minimum force necessary to cleave the cake. If no weight other than the weight of the razor blade and spindle assembly is needed, the caking resistance is still considered excellent. The Examples below show
 5 the grams force of additional weight required to cleave the cake. Cakes requiring less than 200 g force are considered acceptable.

The CIPAC test was used in some of the Examples to measure caking. The CIPAC Method used is MT 172,
 10 "Flowability of Water Dispersible Granules after Heat Test Under Pressure.

The following Examples are presented to illustrate, but not restrict, this invention.

Identity of Ingredients Used in Examples

| <u>Name</u> | <u>Identity</u> |
|---------------------|--|
| Norlig® 11d | calcium lignosulfate (dispersant) |
| Foammaster® Soap L | sodium stearate (anticaking agent) |
| Brij® 700 | polyoxyethylene (100) stearyl ether (anticaking agent) |
| Morwet® D425 | sodium naphthalene formaldehyde condensate (dispersant) |
| Petro® AG-Special | sodium alkyl naphthalene sulfonate (wetting agent) |
| Polyfon® AF | sodium modified kraft lignin (dispersant) |
| Polyplasdone® XL-10 | crosslinked polyvinylpyrrolidone (disintegrant) |
| Aerosol® OT-B | sodium dioctyl sulfosuccinate (anticaking agent) |
| Silwet® L-77 | silicone-polyether copolymer (anticaking agent) |
| Masil® 280LP | silicone surfactant (wetting agent) |
| Wessalon® 50S | precipitated silica (diluent) |

EXAMPLE 1

15 Thirty grams of metsulfuron methyl, 7.5 g of Norlig® 11d, 0.75 g of Foammaster® Soap L, and 93.75 g of potassium sulfate were milled using a Bantam® Mikropulverizer with a 0.027 round hole screen one

pass. The premix and 18 g of Carbowax® PEG 8000 binder (size range = about 37-545 microns, median diameter = 159 microns), were added to a laboratory twin shell (Vee) blender and the blender was tumbled. Heat was added using a laboratory hot air gun and the temperature in the blender was monitored. When the temperature reached 70°C the heat was removed and the tumbling was continued until the temperatures of the granules dropped below 50°C. The granules were then removed from the blender and the product cut was taken by sifting using a laboratory Gilson® sieve shaker fitted with a 14 mesh (1410 microns) and a 200 mesh (74 microns) screen. The 136.2 g of product obtained in this way was a non-dusty, agglomerated granular composition.

PROPERTIES OF GRANULES:

| | |
|--|-------|
| Long Tube Sedimentation (mL, 5 min.) | trace |
| Break-up (s) | 102 |
| Attrition (%) | 19.7 |
| Caking (g) | |
| 0.0, | |
| partially flowed out of cylinder (100 h at 54°C) | |
| After aging 2 weeks at 54°C: | |
| Decomposition of active (%) | <3 |
| Long Tube Sedimentation (mL, 5 min.) | 0 |
| Break-up (s) | 108 |
| Attrition (%) | 25 |

EXAMPLE 2

This composition was prepared by the same process used to prepare that of Example 1. The quantities of each component were the same except that 0.5% (0.75 g) of Witco® calcium stearate was added and 93.00 g of potassium sulfate was used. The calcium stearate was post-blended after the granules were formed and the granulation mass cooled to 50°C. The granulation mass

and the calcium stearate were blended at 50°C for 5 min. before discharging the granules. 145.9 g of 14/200 mesh non-dusty agglomerate-type granules were recovered.

5 PROPERTIES OF GRANULES:

| | | |
|----|--|-------|
| | Long Tube Sedimentation (mL, 5 min.) | trace |
| | Break-up (s) | 48 |
| | Attrition (%) | 1.7 |
| | Caking (g) | |
| 10 | 0.0, | |
| | partially flowed out of cylinder (100 h at 54°C) | |
| | Caking (% through screen) | 78 |
| | after 20 taps according to the CIPAC test | |
| | After aging 2 weeks at 54°C: | |
| 15 | Decomposition of active (%) | <5 |
| | Long Tube Sedimentation (mL, 5 min.) | trace |
| | Break-up (s) | 48 |
| | Attrition (%) | 3.3 |

EXAMPLE 3

20 The active pesticide, 122.1 g of sodium 2-chloro-6-
 [(4,6-dimethoxy-2-pyrimidinyl)thio]benzoate, and 8.1 g
 of potassium sulfate were ground in a CRC® analytical
 laboratory mill. The blend was then added along with
 19.8 g of Carbowax® PEG 8000 to a Vee-blender and the
 25 blender was tumbled. Heat was added using a laboratory
 hot air gun and the temperature in the blender was
 monitored. When the temperature reached 70°C the heat
 was removed and the tumbling was continued until the
 temperatures of the granules dropped below 50°C. The
 30 granules were then removed from the blender and the
 product cut was taken by sifting using a laboratory
 Gilson® sieve shaker fitted with a 14 mesh
 (1410 microns) and a 200 mesh (74 microns) screen.
 133 g of 14/200 mesh granules were obtained.

PROPERTIES OF GRANULES:

| | | |
|---|---|----|
| | Long Tube Sedimentation (mL, 5 min.) | 0 |
| | Break-up (s) | 24 |
| | Attrition (%) | 10 |
| 5 | Caking (% through screen) | 86 |
| | after 20 taps according to the CIPAC test | |

EXAMPLE 4

A composition was prepared by hammermilling 160 g of metsulfuron methyl, 64 g of Norlig® 11d and 488 g of potassium sulfate with a 027 round hole screen. This powder was combined with 88 g of Carbowax® PEG 8000 in a laboratory 2-quart Patterson Kelly® Vee blender. Heat was applied with a laboratory heat gun while the Vee blender was rotating. After reaching 65°C, the heat was turned off and the granules were allowed to cool to less than 50°C while tumbling in the blender. Recovered were 778 g of non-dusty 14/200 mesh granules.

PROPERTIES OF GRANULES:

| | | |
|----|---|-------|
| 20 | Long Tube Sedimentation (mL, 5 min.) | trace |
| | Break-up (s) | 42 |
| | Attrition (%) | 1 |
| | Caking (% through screen) | 48 |
| | after 20 taps according to the CIPAC test | |

25

EXAMPLE 5

Tribenuron methyl sodium salt (50.0 g) and Glacier® talc 325 (10 g) were ground in a CRC® analytical laboratory mill. The powder was then added along with Carbowax® PEG 8000 (15 g) to a Vee blender and granulated as noted in Example 1. 51.9 g of 14/200 mesh granules were obtained (69.2% yield from starting amounts).

PROPERTIES OF GRANULES:

| | | |
|----|--------------------------------------|----|
| | Long Tube Sedimentation (mL, 5 min.) | 0 |
| 35 | Break-up (s) | 36 |

5 EXAMPLE 6

PROPERTIES OF GRANULES:

EXAMPLE 7

PROPERTIES OF GRANULES:

BNSDOCID: <WO 9325074A1 | >

| | |
|---------------------------|-----|
| Attrition (%) | 6.3 |
| Caking (g, 100 h at 54°C) | 100 |

EXAMPLE 8

5 Tribenuron methyl sodium salt (333.0 g), Carbowax®
PEG 8000 (115 g) and 10X sugar (62 g) were combined in
a 2-quart Patterson Kelly® Vee Blender (twin shell)
with intensifier bar. None of the formulation
ingredients were milled. The blender was rotated and
the intensifier bar turned on. Heat was applied using
10 a laboratory heat gun. When the granulation mass
reached 70°C, the heat was turned off and the
intensifier bar was stopped, and the granulation mass
was cooled to less than 50°C. 477.5 g of non-dusty
14/200 mesh granules were recovered.

15 PROPERTIES OF GRANULES:

| | |
|--------------------------------------|-----|
| Long Tube Sedimentation (mL, 5 min.) | 0 |
| Break-up (s) | 54 |
| Attrition (%) | 0.7 |

EXAMPLE 9

20 This Example illustrates melt extrusion of a water-
soluble active ingredient, tribenuron methyl sodium
salt, at 55 wt. % concentration.

300 grams of premix were formulated from the
ingredients listed below. The ingredients were blended
25 and then passed through a MikroPulverizer® hammer
mill. 139 grams of milled premix was slowly added to a
1 inch Wayne® single screw extruder with a 24:1 L/D
ratio. A 2:1 compression ratio screw was used for most
of the runs. The extruder had three electrical heating
30 zones along the barrel plus a band heater for the die.
The feed throat was water-cooled. A mechanical or
electronic pressure indicator was fitted near the end
of the barrel to measure melt pressures close to the
die.

The premix was extruded through a die containing 8 x 0.9 mm holes arranged in a circular pattern. The extrudate consisted of smooth, continuous strands of uniform appearance. The strands were allowed to cool for a few minutes and then were chopped up in a small food processor and screened to obtain the 14 to 35 U.S. sieve cut size.

PREMIX COMPOSITION:

| | <u>Wt. %</u> |
|-------------------------------|--------------|
| tribenuron methyl sodium salt | 55.0 |
| 10 PEG 8000 (Carbowax®) | 22.0 |
| NaHCO ₃ | 3.0 |
| 810 Calcium Carbonate | 20.0 |

EXTRUDER OPERATING CONDITIONS:

Barrel temperature ranges (°C) at:

| | | |
|----|---|-----------|
| 15 | feed zone | 35-49 |
| | transition zone | 55-59 |
| | metering zone | 91-96 |
| | die | 101-108 |
| | Screw Speed (rpm) | 20-30 |
| 20 | Melt Pressure Range (10 ⁶ Pa): | 13.1-31.0 |

PROPERTIES OF GRANULES:

| | | |
|----|---|-------|
| | Long Tube Sedimentation (mL, 5 min.) | 0.004 |
| | Long Tube Sedimentation (mL, 1 week at 54°C) | trace |
| | Untapped Bulk Density (g/l) | 839 |
| 25 | Caking (g) | 0.0, |
| | partially flowed out of cylinder (1 week at 54°C) | |

EXAMPLE 10

The composition of this Example was prepared in the same way as that identical to Example 9 but contains 65 wt. % tribenuron methyl sodium salt. The formulation also contains a dispersant to improve the Long Tube Sedimentation results. 229 g of milled premix was fed into the extruder.

PREMIX COMPOSITION

| | <u>Wt. %</u> |
|-------------------------------|--------------|
| tribenuron methyl sodium salt | 65.0 |
| PEG 8000 (Carbowax®) | 27.0 |
| NaHCO ₃ | 3.0 |
| 5 Morwet® D425 | 1.0 |
| 810 Calcium Carbonate | 4.0 |

EXTRUDER OPERATING CONDITIONS:

Barrel temperature ranges (°C) at:

| | | |
|----|--|-----------|
| | feed zone | 30-39 |
| 10 | transition zone | 48-59 |
| | metering zone | 78-82 |
| | die | 97-98 |
| | Screw Speed (rpm) | 30 |
| | Melt Pressure Range (10 ⁶ Pa) | 22.1-24.8 |

15 PROPERTIES OF GRANULES:

| | | |
|----|--|-------|
| | Long Tube Sedimentation (mL, 5 min.) | 0.0 |
| | Long Tube Sedimentation (mL, 2 weeks at 54°C) | trace |
| | Untapped Bulk Density (g/l) | 769 |
| | Caking (g) | 0.0, |
| 20 | partially flowed out of cylinder (2 weeks at 54°C) | |

EXAMPLE 11

The composition of this Example was prepared by the same process as that of Example 9. This composition contains 70 wt. % tribenuron methyl sodium salt, and a
 25 polyethoxylated alcohol surfactant, Brij® 700, co-melted with the Carbowax® PEG 8000 to help caking performance. No diluent, disintegrant or dispersant are included in this composition. 130 grams of milled premix was fed into the extruder.

30 PREMIX COMPOSITION

| | <u>Wt. %</u> |
|-------------------------------|--------------|
| tribenuron methyl sodium salt | 70.0 |
| PEG 8000 (Carbowax®) | 28.2 |
| Brij® 700 | 1.8 |

EXTRUDER OPERATING CONDITIONS:

Barrel temperature ranges (°C) at:

| | | |
|---|----------------------------------|-----------|
| | feed zone | 29-35 |
| | transition zone | 54-59 |
| 5 | metering zone | 90-91 |
| | die | 97-103 |
| | Screw Speed (rpm) | 30 |
| | Melt Pressure Range (10^6 Pa) | 4.83-13.8 |

PROPERTIES OF GRANULES:

| | | |
|----|---|------|
| 10 | Long Tube Sedimentation (mL, 1 week at 54°C) | 0 |
| | Untapped Bulk Density (g/l) | 735 |
| | Caking (g) | 0.0, |
| | partially flowed out of cylinder (1 week at 54°C) | |

EXAMPLE 12

- 15 This Example illustrates extrusion of the composition of Example 10 without milling the premix. The ingredients were simply blended together and 200 g was then fed into the extruder which provided the necessary mixing and shearing to yield a uniform
- 20 extrudate.

EXTRUDER OPERATING CONDITIONS:

Barrel temperature ranges (°C) at:

| | | |
|----|----------------------------------|-----------|
| | feed zone | 27-32 |
| | transition zone | 49-54 |
| 25 | metering zone | 80-81 |
| | die | 95-97 |
| | Screw Speed (rpm) | 30 |
| | Melt Pressure Range (10^6 Pa) | 22.1-23.4 |

PROPERTIES OF GRANULES:

| | | |
|----|--------------------------------------|-----|
| 30 | Long Tube Sedimentation (mL, 5 min.) | 0.0 |
| | Untapped Bulk Density (g/l) | 762 |

EXAMPLE 13

- This Example illustrates the melt extrusion of a water-insoluble active ingredient, chlorimuron ethyl.
- 35 120 grams of milled premix were fed into the extruder.

A tacky extrudate was obtained which quickly hardened and lost tackiness as it cooled.

| <u>PREMIX COMPOSITION</u> | | <u>Wt. %</u> |
|---------------------------|--|--------------|
| | chlorimuron ethyl | 63.0 |
| 5 | PEG 8000 (Carbowax®) | 16.7 |
| | Aerosol® OT-B | 3.0 |
| | NaHCO ₃ | 3.0 |
| | Polyplasdone® XL-10 | 2.0 |
| | 810 Calcium Carbonate | 12.3 |
| 10 | <u>EXTRUDER OPERATING CONDITIONS:</u> | |
| | Barrel temperature ranges (°C) at: | |
| | feed zone | 32-48 |
| | transition zone | 52-53 |
| | metering zone | 54-55 |
| 15 | die | 60 |
| | Screw Speed (rpm) | 20-30 |
| | Melt Pressure Range (10 ⁶ Pa) | 1.38-4.14 |
| | <u>PROPERTIES OF GRANULES:</u> | |
| | Long Tube Sedimentation (mL, 5 min.) | 0.008 |
| 20 | Long Tube Sedimentation (mL, 1 week at 54°C) | 0.004 |
| | Untapped Bulk Density (g/l) | 756 |
| | Caking (g, 1 week at 54°C) | 201 |

EXAMPLE 14

Five grams of sulfometuron methyl were added to a premelted blend of 4.4 g Carbowax® PEG 8000 and 0.3 g Silwet® L-77 in a small petri dish. To this was added 0.3 g of Petro® AG-Special. The temperature of the slurry was maintained between 90° and 110°C. A pointed spatula was used to deposit a drop of the slurry approximately 1.0 to 2.0 mm in diameter onto a stainless steel plate at room temperature and the drop was allowed to cool completely. This drop-and-cool process was used to make enough "pastilles" to run break-up and caking tests, using granules in the range of 0.85 to 2.0 mm for all tests. After aging for 2

weeks at 54°C, there was only a slight tendency for the pastilles to cake. Also, break-up time was less than 3 min.

EXAMPLE 15

5 Five grams of bensulfuron methyl were added to a premelted blend of 4.7 g Carbowax® PEG 8000 and 0.3 g Silwet® L-77 in a small petri dish. The temperature of the slurry was maintained between 90° and 110°C. A pointed spatula was used to deposit a drop of the
10 slurry approximately 1.0 to 2.0 mm in diameter onto a stainless steel plate at room temperature and the drop was allowed to cool completely. This drop-and-cool process was used to make enough "pastilles" to run break-up and caking tests, using granules in the range
15 of 0.85 to 2.0 mm for all tests. Results of a modified caking test (5 g sample is placed into a 30 mm diameter tube with 150 pounds per square foot loading and aged 100 h at 54°C) show these pastilles to have no caking tendency.

20

EXAMPLE 16

Using the same procedures as described in Examples 14 and 15, 5 g of diuron technical, 4.9 g of Carbowax® PEG 8000 and 0.1 g of Masil® 280LP were used to make the test pastilles. Caking results by the modified
25 100 h/54°C test showed only a very slight, acceptable caking tendency. A break-up test on these granules showed essentially all material fully dispersed in less than 5 min.

EXAMPLE 17

30 Using the same procedures as described in Examples 14 and 15, 5 g of sulfometuron methyl, 4.1 g of Carbowax® PEG 8000, 0.3 g of Silwet® L-77 and 0.6 g of Polyfon® F were used to make the test pastilles. A break-up test on these granules showed complete
35 dispersion within 3 min.

EXAMPLE 18

This example demonstrates dry radial extrusion using Carbowax® PEG 8000 with a water soluble-active ingredient, tribenuron methyl sodium salt at 57% active concentration.

100 grams of premix were formulated from the ingredients listed below. The ingredients were blended and then passed through a CRC mill. The milled premix was then added to a V-blender and heated to 60°C while agitating. The hot premix was then added to the Luwa Benchtop granulator (radial extruder), and the premix was extruded through a 1.0 mm screen. The basket of the granulator was heated with a heat gun before the premix was added for extrusion. A small amount of powder exited the screen before the extrudate started to form. The extrudate consisted of long smooth strands which hardened quickly (1-2 min.). The extrudate was then screened to obtain a 14/60 mesh product cut. The screened extrudate are cylinders approximately 1 mm in diameter and 5 mm in length.

PREMIX COMPOSITION:

| | <u>Wt. %</u> |
|---------------------------------------|--------------|
| PEG 8000 (Carbowax®) | 35 |
| tribenuron methyl sodium salt (92.8%) | 62 |
| Wessalon® 50S | 3 |

PROPERTIES OF GRANULES:

| | |
|--------------------------------------|-------|
| Long Tube Sedimentation (mL, 5 min.) | trace |
| Break-up (s) | 75 |
| Caking (100 h at 54°C) | |

Particles flowed freely from the caking tube with a slight tap.

EXAMPLE 19

This Example demonstrates dry radial extrusion using Carbowax® PEG 8000 with metsulfuron methyl at 18% active concentration. 100 grams of premix were

formulated from the ingredients listed below. The ingredients were blended and then passed through a CRC[®] analytical laboratory mill. The milled premix was then heated in a vacuum oven to 60°C. The hot premix was then added to the Luwa Benchtop granulator (radial extruder). The basket of the granulator was heated with a heat gun before the premix was added for extrusion. The premix was extruded through a 0.8 mm screen. A small amount of powder exited the screen before the extrudate started to form. The extrudate consisted of long smooth strands which hardened quickly (1-2 min.). The extrudate was then screened to obtain a 14/60 mesh product cut. The extrudate was very hard, and had a diameter of 0.8 mm and a length of approximately 5 mm.

PREMIX COMPOSITION:

| | <u>Wt. %</u> |
|--|--------------|
| metsulfuron methyl (97.0%) | 18.0 |
| Norlig [®] 11d | 6.0 |
| anhydrous K ₂ SO ₄ | 50.0 |
| 20 anhydrous Na ₂ CO ₃ | 2.0 |
| anhydrous sodium metaphosphate | 2.0 |
| sugar | 1.0 |
| anhydrous Mg ₂ SO ₄ | 2.0 |
| Carbowax [®] PEG 8000 | 19.0 |

25 PROPERTIES OF GRANULES:

| | |
|--------------------------------------|-------|
| Long Tube Sedimentation (mL, 5 min.) | trace |
| Break-up (s) | 75 |

What is claimed is:

1. A water-dispersible agricultural granular composition in the form of pastilles, agglomerates and heat extrudate granules comprising by weight based on the total weight of the composition:
 - (a) 0.01-90% of one or more active ingredient(s);
 - (b) 1-90% of a water-soluble heat-activated binder selected from one or more of the group consisting of polyethylene glycol molecular weight 6000 to 10,000; polyethylene oxide; polyethoxylated fatty acids and polyethoxylated fatty alcohols; ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols; and
 - (c) optionally additives selected from the group consisting of:
 - (1) 0-10% anticaking agent(s);
 - (2) 0-10% chemical stabilizer(s);
 - (3) 0-20% gas generating disintegrant(s);
 - (4) 0-10% wicking of swelling disintegrant(s);
 - (5) 0-20% dispersant(s);
 - (6) 0-5% wetting agent(s);
 - (7) 0-80% inert diluent(s); and mixtures thereof;
- provided that (i) when the amount of active ingredient(s) and water soluble heat-activated binder together are less than 100% then one or more of the additives are required to bring the composition to 100%; (ii) when the granular composition is in the form of agglomerates the heat activated binder is selected from one or more of polyethylene glycol of average molecular weight of 6000 to 10,000, polyethylene oxide,

and polyethoxylated fatty acids or alcohols; and (iii) when the granular composition is in the form of heat extruded granule the heat activated binder is one or more polyethylene glycol of average molecular weight of
5 6000 to 10,000.

2. The compositions of Claim 1 wherein the amount of active ingredient(s) is 0.03-80% and the amount of water-soluble heat-activated binder is 5-60%.

3. The compositions of Claim 1 wherein the water-soluble heat-activated binder is polyethylene glycol of
10 average molecular weight 6000 to 10,000.

4. The compositions of Claim 2 wherein the water-soluble heat-activated binder is polyethylene glycol of average molecular weight 6000 to 10,000.

5. The compositions of Claim 1 wherein the granular composition is in the form of pastilles and the water-soluble heat-activated binder is selected from one or more of polyethylene glycol of average molecular weight between 6000 to 10,000; ethylene oxide/propylene oxide
15 copolymers; polyethoxylated alkylphenols and polyethoxylated fatty acids and alcohols.
20

6. The compositions of Claim 1 wherein the granular composition is in the form of an agglomerate and the water-soluble heat-activated binder is selected from
25 one or more of polyethylene glycol of average molecular weight between 6000 to 10,000; polyethylene oxide; and polyethoxylated fatty acids and alcohols.

7. A process for preparing a water-dispersible agriculturally suitable granular composition in the
30 form of heat extruded granules comprising by weight based on the total weight of the composition:

- (a) 0.01-90% of one or more active ingredient(s);
- (b) 1-90% of a water-soluble heat-activated
35 binder selected from one or more of the

- group consisting of polyethylene glycol molecular weight 6000 to 10,000, ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols; and
- 5 (c) optionally one or more additives selected from the group consisting of:
- (1) 0-10% anticaking agent(s);
 - (2) 0-10% chemical stabilizer(s);
 - (3) 0-20% gas generating disintegrant(s);
 - 10 (4) 0-10% wicking of swelling disintegrant(s);
 - (5) 0-20% dispersant(s);
 - (6) 0-5% wetting agent(s); and
 - (7) 0-80% inert diluent(s);
- 15 provided that when the amount of active ingredient(s) and water-soluble heat-activated binder together are less than 100% then one or more of the additives are required to bring the composition to 100%, said process comprising feeding a dry premix of the ingredients or
- 20 feeding the ingredients in two or more streams to an extruder with heat supplied either to the premix or the extruder sufficient to soften the heat-activated binder followed by cutting or breaking of the extrudate to form granules.
- 25 8. The process of Claim 7 wherein the ingredients are separated in two or more streams.
9. The process of Claim 8 wherein the ingredients are heated from 45° to 130°C in the extruder.
10. The process of Claim 8 wherein the heat-
- 30 activated binder is polyethylene glycol of average molecular weight of 6000 to 10,000.

INTERNATIONAL SEARCH REPORT

PCT/US 93/05371

International Application No

| | | |
|--|--|-------------------------------------|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| Int.Cl. 5 A01N25/14 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁷ | | |
| Classification System | Classification Symbols | |
| Int.Cl. 5 | A01N ; B01J | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ | | |
| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
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| <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report | |
| 27 SEPTEMBER 1993 | 13. 10. 93 | |
| International Searching Authority | Signature of Authorized Officer | |
| EUROPEAN PATENT OFFICE | MÜLLNERS W. | |

Form PCT/ISA/210 (second sheet) (January 1985)

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| X | FR,A,2 645 709 (SUMITOMO CHEMICAL COMPANY) 19 October 1990 see page 2, line 11 - line 21 see page 3, line 25 - page 4, line 31 see page 11, line 8 - line 17; claim 1 ----- | 1-4 |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9305371
SA 75883

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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27/09/93

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